CHAPTER 7

Atmospheric Deposition of Sulfur and Nitrogen Compounds

http://www.epa.gov/oar/aqtrnd98/chapter7.pdf

Sulfur and nitrogen oxides are emitted into the atmosphere primarily from the burning of fossil fuels. These emissions react in the atmosphere to form compounds that are transported long distances and are subsequently deposited in the form of pollutants such as particulate matter (sulfates, nitrates) and related gases (nitrogen dioxide, sulfur dioxide and nitric acid). Nitrogen oxides will also interact with volatile organic compounds to form ozone. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity. Toxic pollutants and metals can also be transported and deposited through atmospheric processes. (See Chapter 5: Air Toxics.)

Both local and long-range emission sources contribute to atmospheric deposition. Total atmospheric deposition is determined using both wet and dry deposition measurements. Wet deposition is the portion dissolved in cloud droplets and is deposited during rain or other forms of precipitation. Dry deposition is the portion deposited on dry surfaces during periods of no precipitation as particles or in a gaseous form. Although the term "acid rain" is widely recognized, the dry deposition portion can range from 20–60 percent of total deposition.

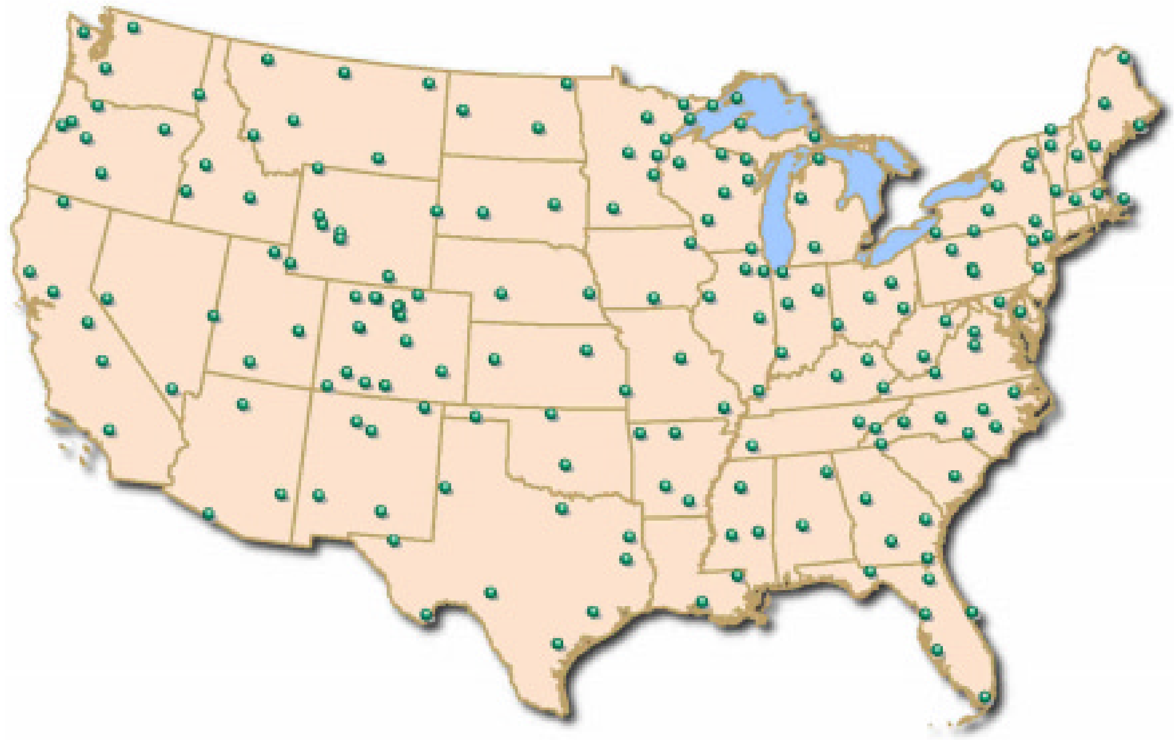
EPA is required by several Congressional and other mandates to assess the effectiveness of air pollution control efforts. These mandates include Title IX of the Clean Air Act Amendments (the National Acid Precipitation Assessment Program), the Government Performance and Results Act, and the U.S./Canada Air Quality Agreement. One measure of effectiveness of these efforts is whether sustained reductions in the amount of atmospheric deposition over broad geographic regions are occurring. However, changes in the atmosphere happen very slowly and trends are often obscured by the wide variability of measurements and climate. Numerous years of continuous and consistent data are required to overcome this variability, making long-term monitoring networks especially critical for characterizing deposition levels and identifying relationships among emissions, atmospheric loadings and effects on human health and the environment.

For wet and dry deposition, these studies typically include measurement of concentration levels of key chemical components as well as precipitation amounts. For dry deposition, analyses must also include meteorological measurements that are used to estimate rate of the actual deposition, or "flux." Data representing total deposition loadings (e.g., total sulfate or nitrate) are what many environmental scientists use for integrated ecological assessments.

Primary Atmospheric Deposition Monitoring Networks

The National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNet) were developed to monitor wet and dry acid deposition, respectively. Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNet also includes measurements of rural ozone and the

Figure 7-1. The NADP/NTN Network.



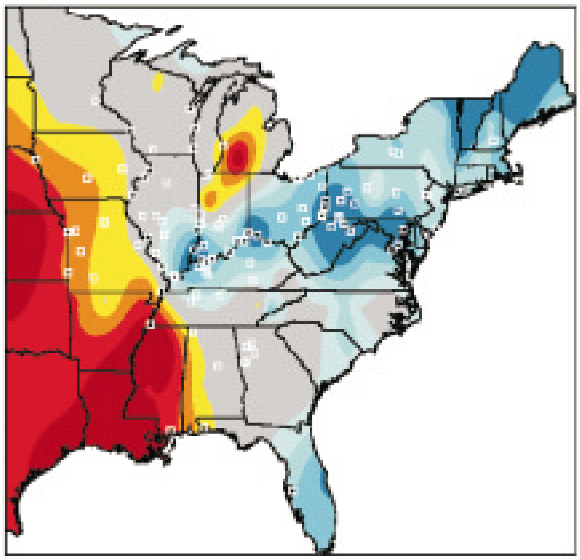
chemical constituents of $PM_{2.5}$. Rural monitoring sites of NADP and CASTNet provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal. These data provide needed information to scientists and policy analysts to study and evaluate numerous environmental effects, particularly those caused by regional sources of emissions for which long range transport plays an important role. Measurements from these networks are also important for understanding non-ecological impacts of air pollution such as visibility impairment and damage to materials, particularly those of cultural and historical importance.

National Atmospheric Deposition Network

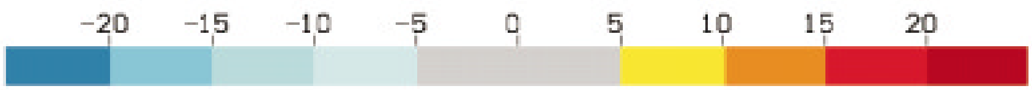
The National Atmospheric Deposition Program (NADP) was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, and electric utilities and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Collection of weekly wet deposition samples began in 1978. The size of the NADP Network grew rapidly in the early 1980s when the major research effort by the National Acid Precipitation Assessment Program (NAPAP) called for characterization of acid deposition levels. At that time, the network became known as the NADP/NTN (National Trends Network). By the mid-1980s, the NADP had grown to nearly 200 sites, where it stands today as the longest running national deposition monitoring network (see Figure 7-1).

The NADP analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The Network measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by NADP's Central Analytical Lab at the Illinois State Water Survey. A new subnetwork of the NADP, the Mercury Deposition Network (MDN) measures mercury in precipitation. For more information on the MDN, see Chapter 5: Air Toxics.

Figure 7-2. Percent differences in mean annual measured sulfate concentrations as compared to projected concentrations for 1995–1996 for the eastern United States (from NADP/NTN).



Small squares on the map show locations of electric utility plants affected under Phase I of the Acid Rain Program. Areas on the map depicting higher sulfate concentrations (e.g., south and east of Lake Michigan and the southwestern portion of map) appear to be due to below average precipitation volumes, which are associated with higher concentrations of sulfate. In addition, these results may have been affected by SO_2 emission increases at some Phase II emissions sources that are controlled by the Acid Rain Program in the year 2000.



Trends Analyses for Sulfate and Nitrate Concentrations in Wet Deposition

Table 7-1. Mean Annual Sulfate Wet Deposition, 1989–1998, in Three Sensitive Regions in the Eastern United States

Region	Mean Annual Sulfate Wet Deposition (kg/ha) (1989–91	1995–98)	Percent Change in Mean Annual Sulfate Wet Deposition (1989–91 to 1995–98)
Adirondacks	25.6	18.9	-26
Mid-Appalachian	27.3	21.4	-21
Southern Blue Ridge	22.9	19.6	-15

Sulfate concentrations in precipitation have decreased over the past two decades.[1] The reductions were relatively large in the early 1980s followed by more moderate declines until 1995. These reductions in wet sulfates are similar to changes in SO_2 emissions. In 1995 and 1996, however, concentrations of sulfates in precipitation over a large area of the eastern United States exhibited a dramatic and unprecedented reduction. Sulfates have been estimated to be 10–25 percent lower than levels expected with a continuation of 1983–1994 trends (see Figure 7-2). This important reduction in acid precipitation is directly related to the large regional decreases in SO_2 emissions resulting from phase I of the Acid Rain Program (See "Trends in SO_2" in Chapter 2 of this report). The largest reductions in sulfate concentrations occurred along the Ohio River Valley and in states immediately downwind of this region. For example, the average reduction in sulfate concentrations in Ohio was approximately 21 percent, in Maryland 27 percent, and in Pennsylvania 15 percent. The largest decrease (32 percent) occurred in the northern portion of West Virginia. Reductions in hydrogen ion concentrations in the East, the primary indicator of precipitation acidity, were very similar to those of sulfate concentrations, both in magnitude and location. Nitrate concentrations at NADP/NTN sites were not appreciably different in 1995–1996 from historical levels.[2]

The effects of decreased SO_2 emissions on sulfates can also be seen by comparing deposition maps for the eastern United States. Figures 7-3a and 7-3b compare wet sulfate deposition between 1989–1991 and 1995–1998.[3] The sulfate concentrations in precipitation are still highest in the Great Lake states and areas extending eastward, but the magnitude of the levels are greatly reduced.

The percent improvement between 1989–1991 and 1995–1998 can also be viewed in terms of three sensitive regions in the eastern United States: Adirondacks, Mid-Appalachians, and Southern Blue Ridge. Table 7-1 shows that the improvements range from 15–26 percent. The largest improvements were in the Adirondacks and Mid-Appalachians.[3]

Figure 7-3a. Trends in wet sulfate deposition (kg/ha); 1995–1997.

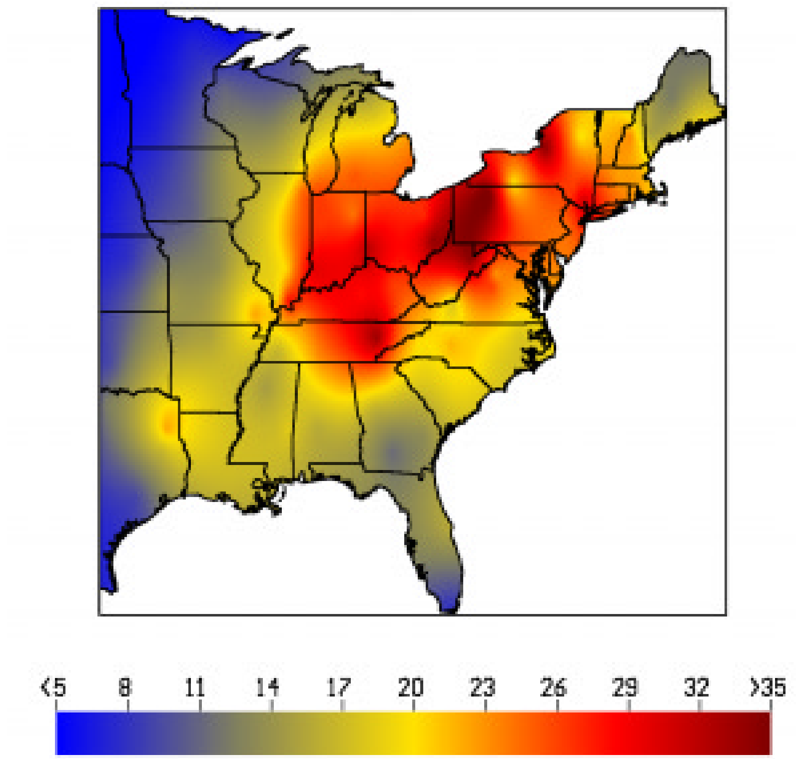
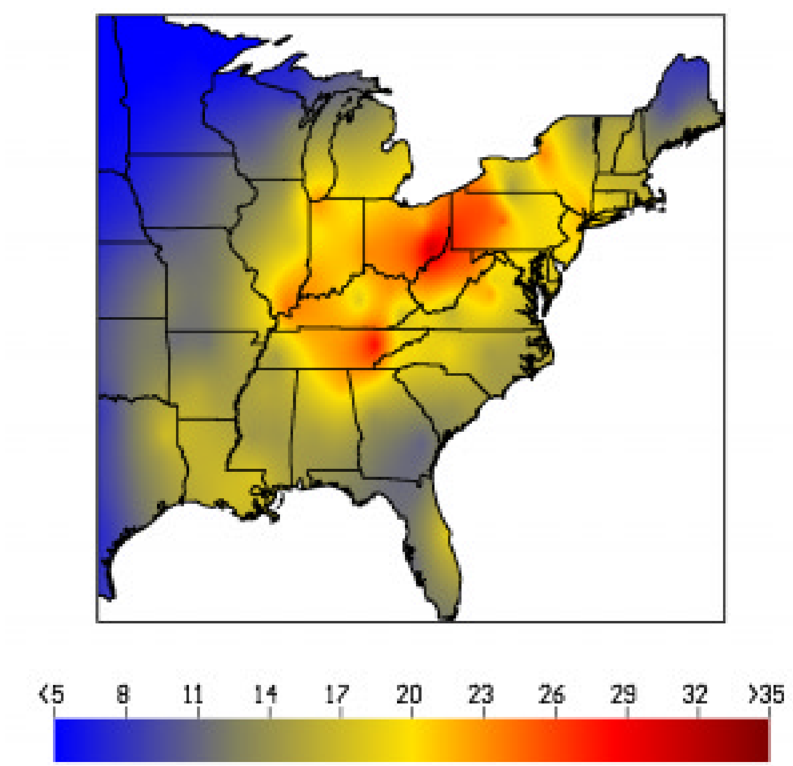


Figure 7-3b. Trends in wet sulfate deposition (kg/ha); 1989–1991.

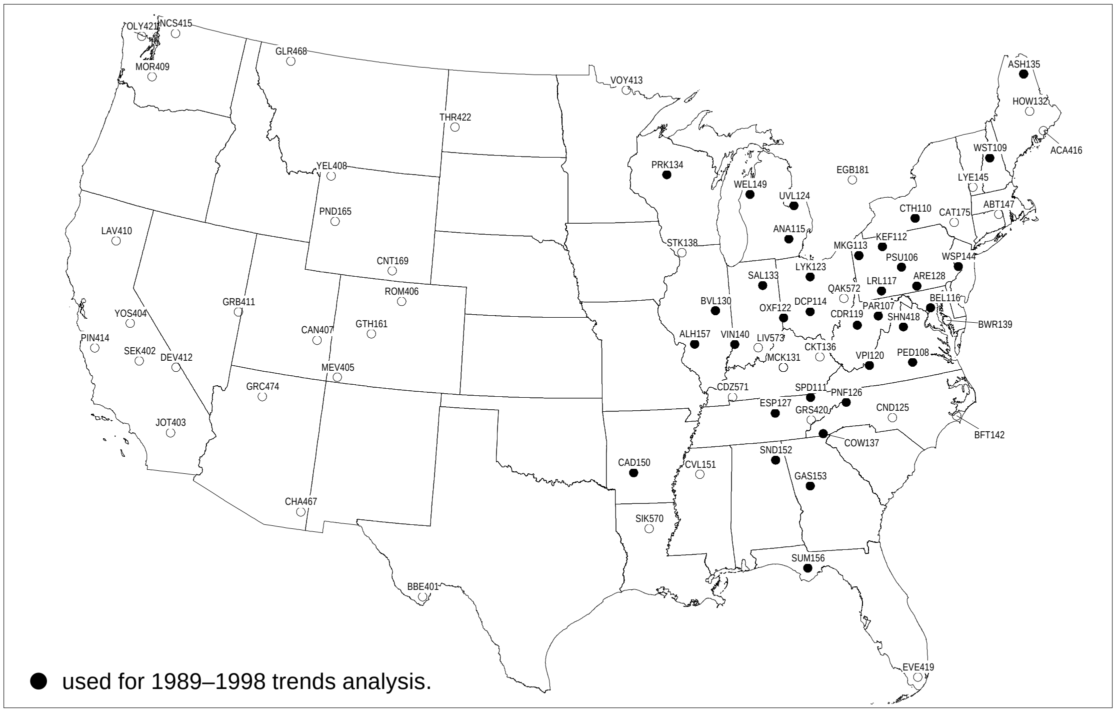


Clean Air Status and Trends Network

The Clean Air Status and Trends Network provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone and other forms of atmospheric pollution. CASTNet is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNet is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNet now comprises 79 monitoring stations across the United States. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, 27 stations are operated by the National Park Service (NPS) in cooperation with EPA. Of the total number of sites, 74 measure dry-deposition, 19 measure wet-deposition, 68 measure ozone, and eight measure aerosols for visibility assessment.

Each CASTNet dry deposition station measures:

Figure 7-4. CASTNet Network and subset of 34 sites used for 1989–1998 trends analysis.



- Weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid (sulfate, nitrate and ammonium generally exist as fine particles).
- Hourly concentrations of ambient ozone levels.
- Meteorological conditions required for calculating dry deposition rates.

Dry Deposition

Dry deposition rates are calculated using atmospheric concentrations, meteorological data and information on land use, vegetation, and surface conditions. CASTNet complements the database compiled by NADP. Because of the interdependence of wet and dry deposition, CASTNet also collected wet deposition data at the 18 sites where there are no NADP/NTN stations within a 50 km radius. Now, these sites are officially part of the NADP. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition. NOAA also operates a smaller dry deposition network called Atmospheric Integrated Assessment Monitoring Network (AIRMoN) focused on addressing research issues specifically related to dry deposition measurement.

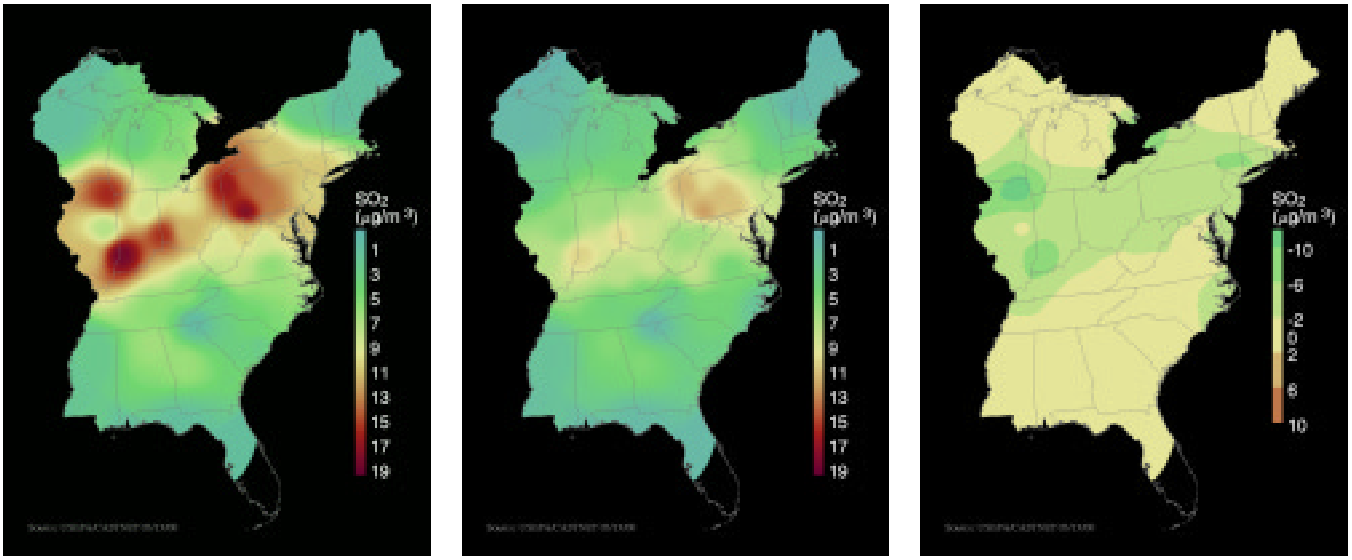
Concentration Trends Analysis at CASTNet Sites

CASTNet ambient concentration data in the eastern United States were analyzed for the period 1989 to 1998 for the change in ambient sulfur dioxide, sulfates, total nitrates and ammonium. First, maps are presented for a comparison of 2-year periods at the beginning and end of the 10-year period based on data from all 50 eastern locations in the CASTNet monitoring program. Then data from a subset of 34 Eastern CASTNet sites with the most complete historical record are examined for year to year changes from 1989 to 1998.[5]

In the early 1990s, ambient SO_2 concentrations in the rural eastern United States were highest in western Pennsylvania, along the Ohio Valley and in the vicinity of Chicago/Gary Indiana. Large improvement in SO_2 air quality can be seen by comparing 1990–1991 with 1997–1998. The largest decreases in concentrations are noted in the vicinity of Chicago and throughout the states bordering the Ohio Valley (IL, IN, OH, PA, KY, WV). The highest SO_2 concentrations in the rural parts of the eastern United States are now concentrated in southwestern PA.

In the early 1990s, sulfate concentrations greater than 5 $\mu g/m^{3*}$ cover

Figure 7-5a. Comparison of ambient sulfur dioxide concentrations in the rural eastern United States from CASTNet monitoring data, 1990–1991 vs. 1997–1998



1990–1991

1997–1998

Decrease in ambient sulfur dioxide concentrations in the rural eastern United States, 1990–1991 vs. 1997–1998.

most of the eastern United States. Regions of concentrations greater than 6 µg/m^3 are estimated to cover the Ohio Valley States (Il, IN, OH, KY, WV), PA and the other mid-Atlantic states from New Jersey to Virginia. The highest sulfate concentrations (> 7 µg/m^3) were adjacent to the Ohio Valley and in northern Alabama. These are the locations of large electric utilities.

In the late 1990s (represented by the period 1997–1998), sulfates were dramatically lower. Although there are differences between 1997 and 1998, as discussed below, both the size of the region with and the magnitude of the highest concentrations has decreased. However, the region with concentrations higher than 5 µg/m^3 does not appear to have changed appreciably.

The location of all CASTNet sites and those used for the 10-year trend analysis are shown in Figure 7-4. During this 10-year period, atmospheric concentrations of SO_2 and sulfate both showed statistically-significant declining trends. The average reduction in the these rural sulfur dioxide and sulfate levels was 38 percent** and 22 percent respectively. The distribution of annual average concentrations is presented as box-plots in Figures 7-6 and 7-7. An average 10-percent increase in sulfates between 1997 and 1998 is also noted.

The trend in total nitrate concentrations (nitrates plus nitric acid) was essentially flat, corresponding to the small change in NO_x emissions during this period. The highest nitrate concentrations are found in the States of Ohio, Indiana and Illinois.

Ammonium concentrations in the ambient air are typically associated with sulfate and nitrate compounds. The ammonium maps presented in Figure 7-5d show that the highest ammonium concentrations are also highest in the midwest. However, the decrease in ambient ammonium over the 10-year period primarily occurred in the Ohio Valley and appears to be associated with the reduction in sulfate concentrations.

Electric utilities account for 71 percent of the SO_2 emissions in the eastern United States. However, they accounted for most of the nationwide reduction in SO_2 emissions.[7] The trend in ambient sulfates and sulfur

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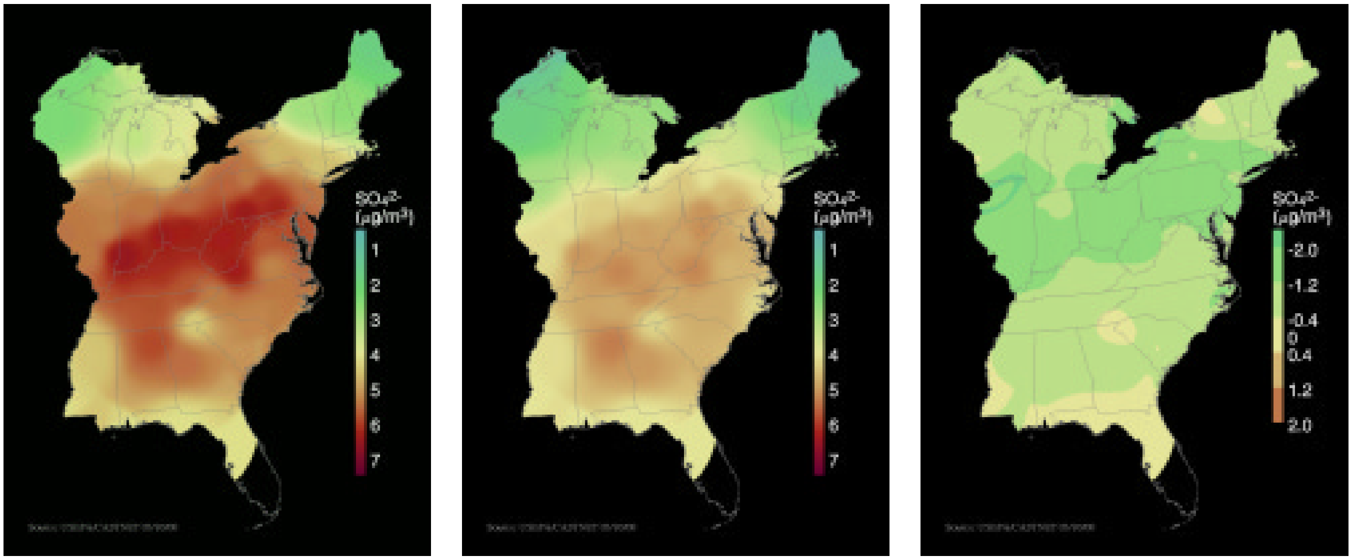
*Sulfate concentrations represent the sulfate ion, SO_4^{-2}, and do not represent the compounds (i.e., ammonium sulfate or ammonium bisulfate) typically associated with this analyte.

**The overall 38-percent decline in ambient SO_2 concentrations in rural areas matches the national air quality improvement in urban areas as measured by the state and local air monitoring stations.

Figure 7-5b. Comparison of ambient sulfate concentrations in the rural eastern United States from CASTNet monitoring data, 1990–1991 vs. 1997–1998.

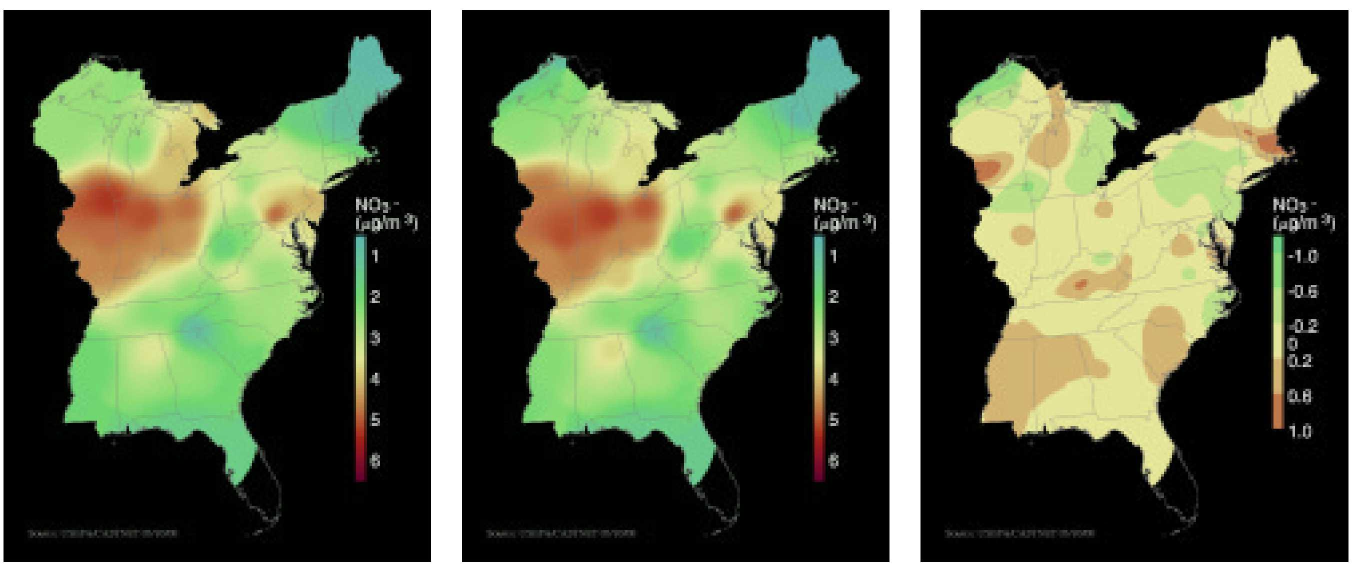


1990–1991

1997–1998

Decrease in ambient sulfate concentrations in the rural eastern United States, 1990–1991 vs. 1997–1998.

Figure 7-5c. Comparison of ambient total nitrate concentrations in the rural eastern United States from CASTNet data, 1990–1991 vs. 1997–1998.

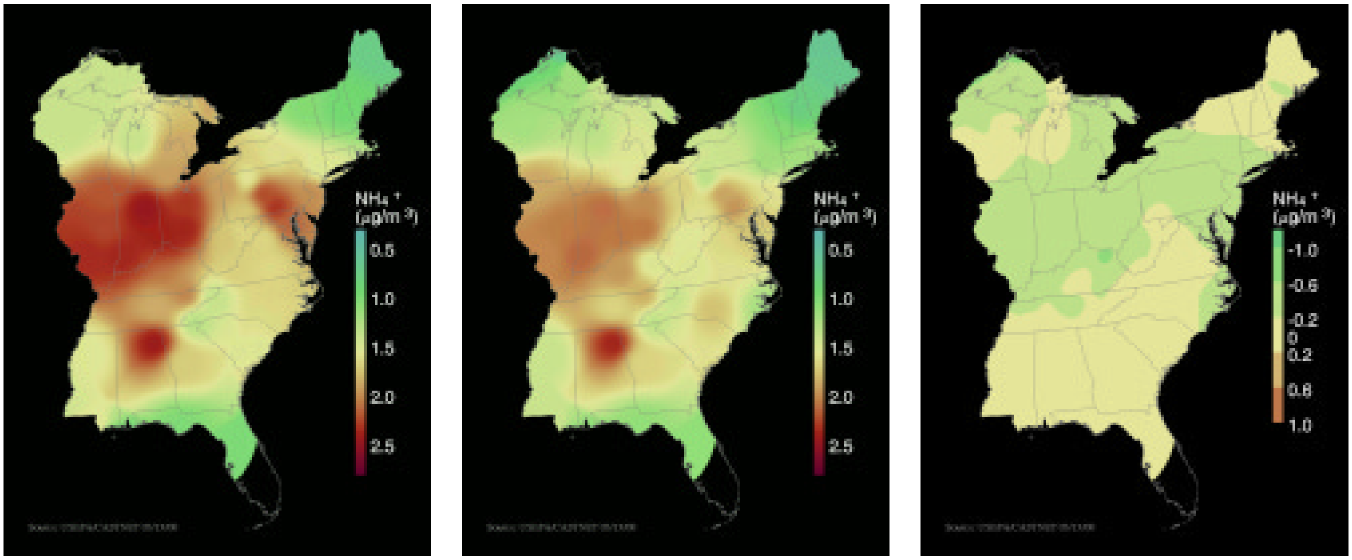


1990–1991

1997–1998

Decrease in ambient total nitrate concentrations in the rural eastern United States, 1990–1991 vs. 1997–1998.

Figure 7-5d. Comparison of ambient ammonium concentrations in the rural eastern United States from CASTNet data, 1990–1991 vs. 1997–1998.



1990–1991

1997–1998

Decrease in ambient ammonium concentrations in the rural eastern United States, 1990–1991 vs. 1997–1998.

dioxide are generally consistent with the change in annual sulfur dioxide emissions from electric utilities in the eastern United States. Figure 7-8 shows that the 22 percent 10-year decline in sulfates matches the overall 21-percent decline in SO_2 emissions. In addition, the 1997–1998 increase in ambient sulfates (10 percent) appears to follow the 5-percent increase in annual emissions.

Figure 7-9 presents the trends in ambient sulfates, ambient sulfur dioxide, and SO_2 emissions by calendar quarter. Most of the increase in emissions and ambient sulfates occurred during the high sulfate "season" (i.e., the 2nd and 3rd calendar quarters). This season with its slow moving air masses and high photochemical activity contributes 65–70 percent to the typical annual average

Figure 7-6. Trend in ambient sulfates in the rural eastern United States, based on CASTNet monitoring data, 1989–1998.

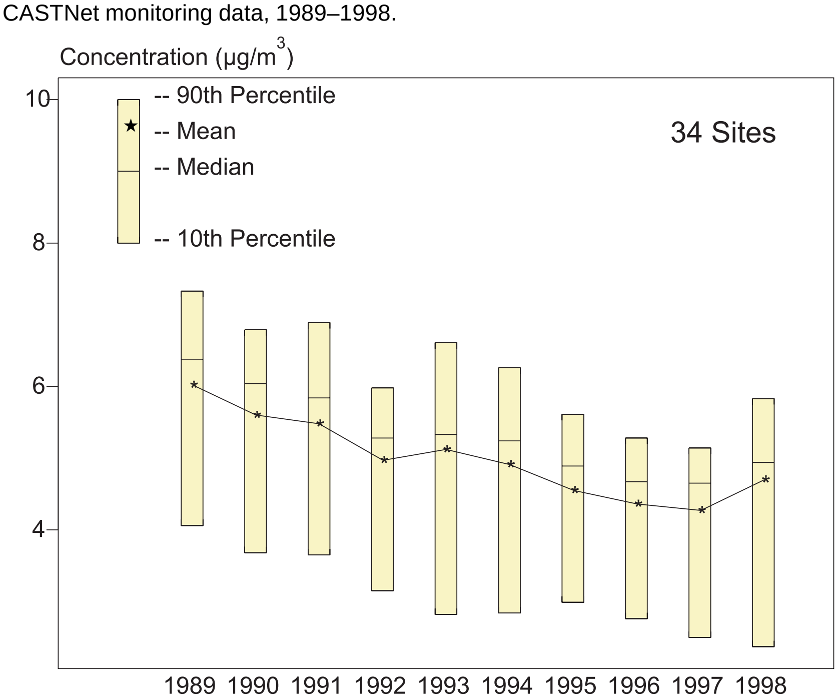


Figure 7-7. Trend in ambient sulfur dioxide in the rural United States, based on CASTNet monitoring data, 1989–1998.

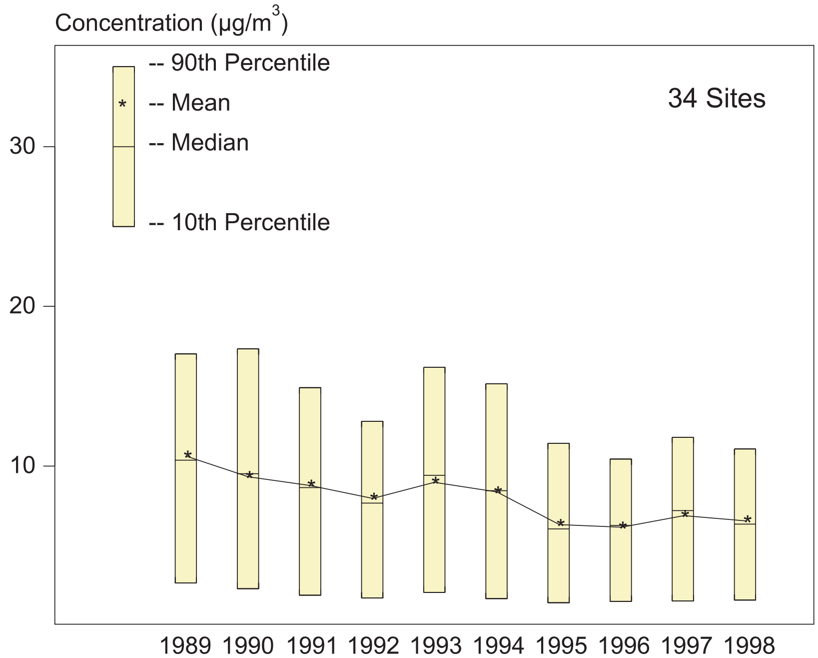
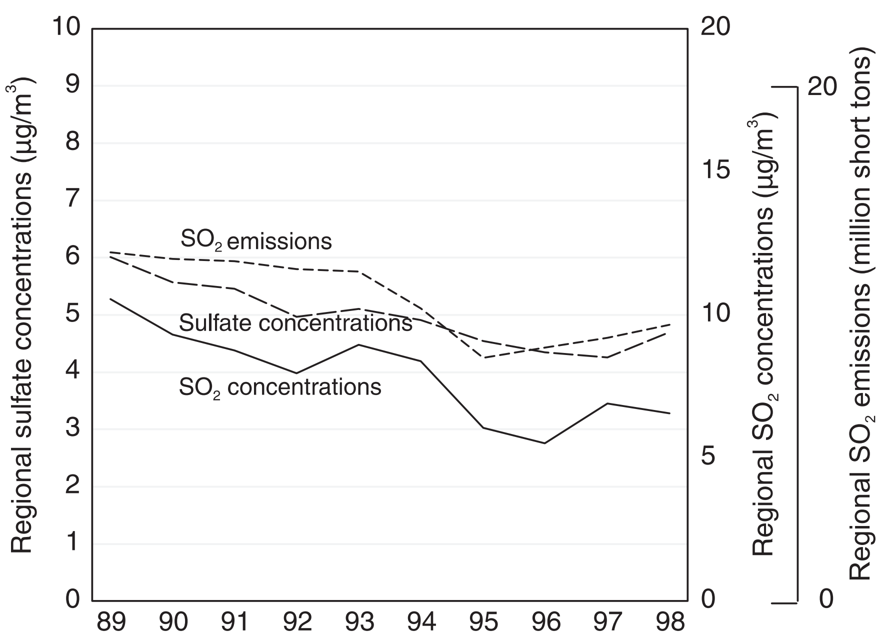


Figure 7-8. Trend in annual average ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO_2 emissions from electric utilities in rural eastern United States, 1989–1998.



concentrations of sulfates. It also has slightly more than half of the annual SO_2 emissions. Between these warmer months of 1997 and 1998, regional sulfur dioxide emissions increased 12 percent between 1997 and 1998 and average sulfates increased 21 percent. The higher summertime emissions in 1998 are attributed in part to the extra demands on electric utilities due to extremely warm temperatures throughout the Southeast (see Figure 2-27 in the ozone section of Chapter 2.)

For annual average ambient sulfur dioxide, the trend appears to better mimic the large drop in regional emissions which occurred between 1993 and 1995. The 10-year improvement in rural ambient SO_2 levels in eastern United States was also more substantial than the 10-year decrease in regional emissions. Unlike sulfates, however, ambient SO_2 is highest during the colder months (i.e., 1st and 4th calendar quarters) and most of the 10-year decrease in ambient SO_2 occurred during these quarters. From 1989–1998, the 6-cold-month average SO_2 concentrations (now accounting for 60–65 percent of the annual average) decreased 44 percent. The 10-year decline in emissions, -29 percent, was also greater during the colder months. During the last two years, annual average SO_2 decreased while annual emissions increased. However, air quality and emissions match more closely on a seasonal basis. During the cold months, average SO_2 concentrations and total emissions increased slightly in the 1st quarter but decreased during the latter part of the year. For the warmer months (the 2nd and 3rd calendar quarters), the figure reveals a large increase in SO_2 emissions, ambient sulfates and ambient sulfur dioxide between 1997 and 1998 during. (See the criteria pollutants section in Chapter 2 for more information about SO_2 emission trends and the acid rain program. Also see **www.epa.gov/acidrain/**).

References

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2. Lynch, J.A., V.C Bowersox and J.W. Grim. 1996. *Trends in Precipitation Chemistry in the United States: An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV*. U.S. Geological Survey. Open-file Report 96-0346.

3. "Changes in Sulfate Deposition in the Eastern USA Following Enactment of Title IV of the Clean Air Act Amendments of 1990." Lynch, J.A., Bowersox, V.C. and Grimm, J.W., 1999. *Atmospheric Environment.* In Press.

4. Holland, D. P. Principe and J. Sickles, II. 1998. In press, *Atmospheric Environment*.

5. Clean Air Status and Trends Network (CASTNet), *1998 Annual Report*. **<http://www.epa.gov/acidrain/castnet/annual98/annual98.html>**

6. The overall 38-percent decline in ambient SO_2 concentrations in rural areas matches the national air quality improvement in urban areas as measured by the State and local air monitoring stations.

7. Eighty-four percent of the 10-year nationwide reduction in SO_2 emissions is attributed to fuel combustion from electric utilities.

Figure 7-9a. Trend in annual average ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO_2 emissions from electric utilities in rural eastern United States by calendar quarter, 1989–1998; quarter 1.

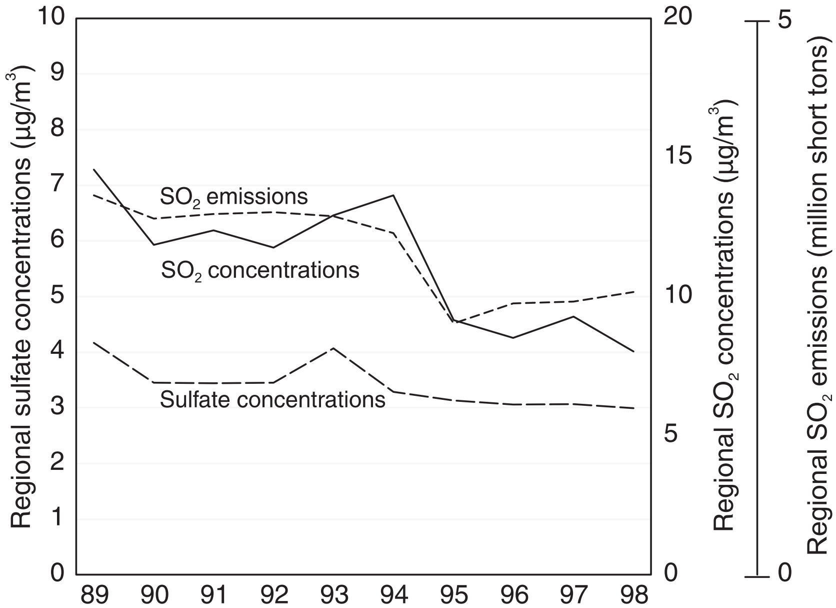

Figure 7-9b. Trend in annual average ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO_2 emissions from electric utilities in rural eastern United States by calendar quarter, 1989–1998; quarter 2.

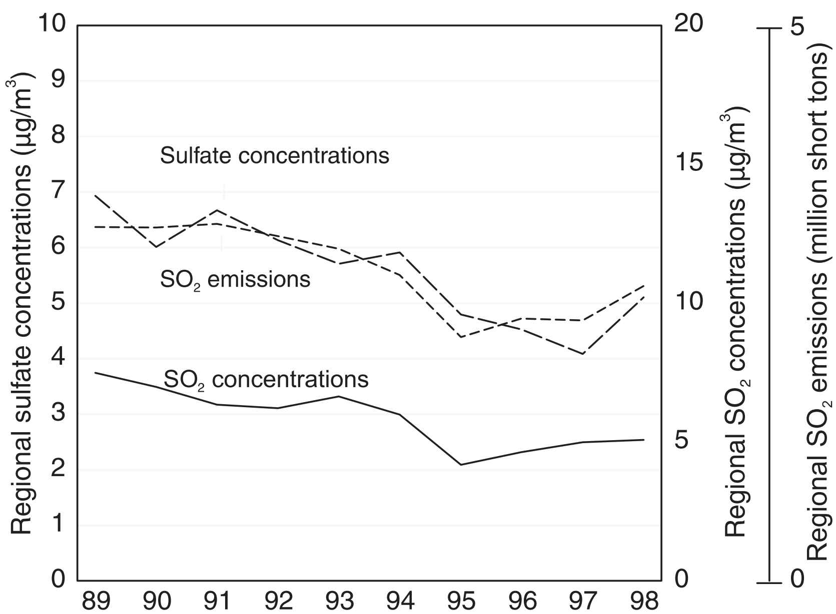

Figure 7-9c. Trend in annual average ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO_2 emissions from electric utilities in rural eastern United States by calendar quarter, 1989–1998; quarter 3.

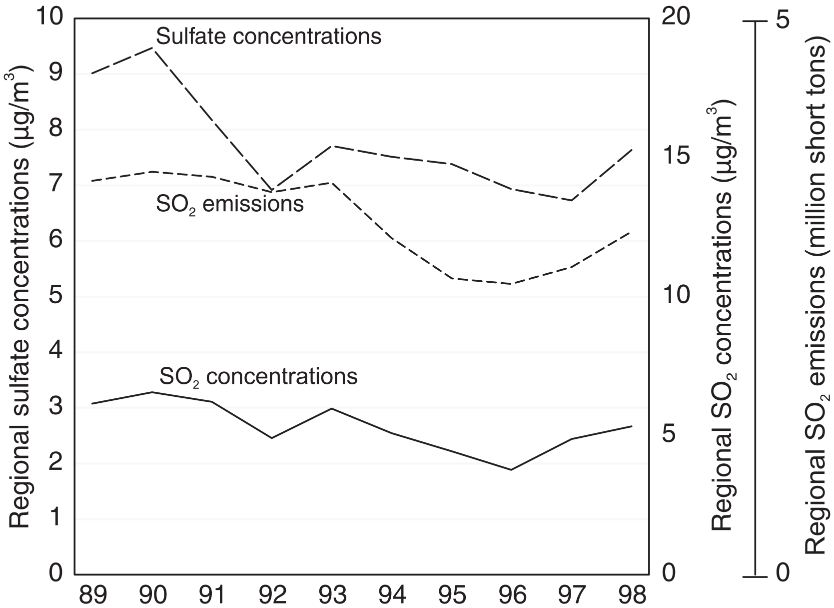

Figure 7-9d. Trend in annual average ambient sulfur dioxide and sulfate concentrations, based on CASTNet monitoring data, and regional SO_2 emissions from electric utilities in rural eastern United States by calendar quarter, 1989–1998; quarter 4.